

Final Report

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Bacterial Electrochemical Asymmetry PotentialPurpose of Project

This project was undertaken in an attempt to learn the source of a large (ca. 1 V) potential difference that develops between two "identical" noble metal electrodes during (E-coli) bacterial growth in closed culture tubes. Previous work had shown such response with platinum and other noble metal electrodes as well as with bimetallic systems.

An electrochemical explanation for the phenomena has been found and the hypothesis tested. Upon identification of the probable cause, the major effort was directed to a better understanding of certain fundamental relationships concerning cell potentials, energy changes and the thermodynamic relationships that govern and/or may be derived from electrochemical phenomena.

Probable Source of the Voltage

The major factors affecting the potential in such systems have been identified as redox surface changes on electrodes associated with the depletion of oxygen in the system as the bacteria reach maximum growth rates. Whether the maximum growth rate was limited by oxygen or other factors was not examined, although the former is likely, since the bacteria, although facultative, grow at a much slower rate in anaerobic conditions. The rapid growth evidently generates local variations in oxygen content and in byproduct concentrations, including reducing gases.

The procedure and results of the experiments followed in determining the source of the asymmetry has been described previously (see interim report of 16 January, 1987) and are summarized here. Platinum electrodes contain a monolayer of oxygen atoms under all but reducing conditions. As the oxygen concentration is reduced the platinum electrode begins to respond to redox couples other than PtO/Pt , particularly to $\text{H}^+(\text{aq})/\text{H}_2$ couple where hydrogen gas is being produced. If this occurs at different times at the two electrodes differences in potential of about one volt between the electrodes will result. This explanation was verified by determining potentials of each electrode vs. a reference electrode under various redox conditions created by bubbling hydrogen, nitrogen or oxygen through the

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reaction chamber. In such cases, responses similar to those obtained during bacterial growth were seen. Note that the potentials are, in a sense, an artifact of the high impedance of the recorders commonly used for such measurements; at lower impedance the electrodes will reach a state of equilibrium due to electron transfer. This was found to be true as current measurements were attempted with various electrodes - the voltage falls, as expected, as current flows between them.

It had been proposed that this developing potential could be used to monitor bacterial growth in environmental settings. The onset of the potential increase does correspond with a maximum in the growth rate of the bacteria. The use of this detection method as a monitor for bacterial concentrations in the environment, however, appears impractical unless some way is found to distinguish the effects of the bacteria from other point sources of anaerobic conditions. We have not tested whether similar results with bacteria would be obtained in an open system, with exposure to atmospheric oxygen during bacterial growth and significant mixing. While it is likely that the redox condition of an environmental system could be effectively monitored electrochemically, use of a single indicator electrode with a suitable reference electrode would accomplish the same result, as is done when oxygen levels are monitored with currently available oxygen electrodes.

Thermodynamic Considerations

The second phase of this project concerns related thermodynamic considerations. Two relationships allow a direct route to explanation of free energy, the first is the Nernst equation, $E = E^\circ - (RT/nF) \ln Q$, and the identification of free energy with cell potential, $\Delta G = -nFE$; from these the relationship between free energy change and activities can be found directly. Consideration of the meaning of "free energy" has led to a different approach to thermodynamics that provides more direct explanations for physical behavior involving not only electron transfer but other processes as well. In contrast with current presentations, it does not invoke certain restrictions on the meaning of "energy" that currently necessitate several different energy functions (such as free energy). Some fundamental assumptions of current presentations are

challenged. For example, consideration of the differential equations for changes in an ideal gas demonstrates that energy of an ideal gas cannot be a function of temperature alone:

$$\text{For } E = E(P,T),$$

$$dE = (\partial E/\partial P)dP + (\partial E/\partial T)dT;$$

$$\begin{aligned} \text{but for an ideal gas, } (\partial E/\partial T)dT &= (\partial E/\partial P)(\partial P/\partial T)[d(PV/nR)] \\ &= (\partial E/\partial P)dP. \end{aligned}$$

Thus, the energy of an ideal gas can be expressed equally as well as a function of temperature or pressure. The convenience of temperature measurement over that of pressure does not alter the equivalency of the two dependences of energy. Consequences of this "obvious" mathematical relationship are rather significant in developing a different approach. Among other findings, the new approach helps explain the nature of the entropy function and why it is unnecessary in determining spontaneity (or for any other purpose in the new approach). Since the energy of an ideal gas is currently said to be a function of temperature alone, it is necessary to interpret all driving forces for all processes involving ideal gases to a difference in temperature (or, equivalently, to the absolute temperature). Thus, a pressure difference between two gas samples at the same temperature must be interpreted in terms of the equivalent driving force resulting from a temperature difference. This rather complicated reasoning derived from historical developments that were in many cases misinterpreted and often so remain (for example, Joule's "mechanical equivalent of heat").

The reconsideration of some postulates of current thermodynamic presentations leads to questions about the basic premises. The following aspects of current presentations have been considered:

1. Energy as a state function.

If we accept the definition of energy as "the ability to do work", then it follows that the energy of a system cannot be specified without stipulation of the second system upon which the work will be expended. The lack of such relativistic consideration for the energy of a system reflects the origins of thermodynamics, prior to the introduction of such relativistic factors into energy calculations. One would not currently refer to kinetic energy without stipulating the frame of reference; similarly, no meaningful discussion of "energy" of a system can legitimately

exclude consideration of the force against which work is to be done (or, equivalently, the temperature of the surroundings which will heat or be heated by the system). It is shown that it is energy transfer, not energy itself that is conserved; hence, "Conservation of Energy", as currently used, is not a valid premise. That this is so is directly seen in considering the return toward equilibrium of any system with "potential energy"; the ability to do work decreases in the course of the process, hence energy is destroyed. That a temperature increase may occur does not change the direct evidence. The ability of that temperature increase to relate to work depends on there being another system at lower temperature to which energy can be transmitted; hence, once more, the relativistic nature of energy is seen.

2. The energy of an ideal gas is a function only of its temperature.

A novel piston-in-cylinder model is used to demonstrate that both temperature and pressure can represent the energy of an ideal gas; that neither alone can adequately describe the energy of the gas, and that, current presentations notwithstanding, a "spontaneous" increase in temperature of a system can readily be achieved (as is done in any adiabatic compression). The matter can be analyzed directly by considering the following question: can a compressed gas do more work than the same gas expanded isothermally into a larger volume. The answer, of course, is affirmative. This requires that derivations for isothermal, isobaric, isochoric and adiabatic changes for an ideal gas (or any other substance) be reconsidered. This has been done; the new derivations provide more direct routes to the needed relationships.

3. Criteria for spontaneity

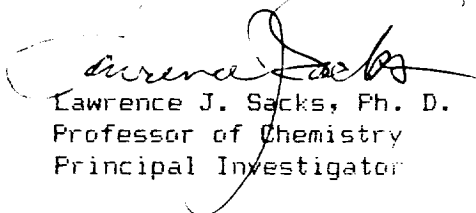
Current criteria for spontaneous, non-spontaneous and equilibrium changes are based on positive, negative and zero entropy changes. These are replaced in the new approach by direct consideration of energy changes. A spontaneous change involves loss of energy; an anti-spontaneous change occurs with a net energy gain; and equilibrium processes occur under conditions of constant energy. This set of conditions constitutes a new Second Law. From it, relationships for the usual changes in configuration of an ideal gas are directly derived.

4. Other relationships

Energy changes for isothermal and adiabatic compressions have been calculated using a simplified version of kinetic theory, in which an average molecule is used instead of a statistical assemblage. Both "reversible" and "irreversible" processes are equally well treated and results give greater insight into the nature of the so-called irreversible processes. Current stipulations with respect to very slow compression of "weightless" pistons and friction-free processes are found to be extraneous for most processes. Deviations at high piston velocity are seen to be a function of the nature of energy transfer in isothermal changes and of energy randomization in adiabatic changes.

Acknowledgment

The author wishes to express his appreciation to NASA-LaRC for support of this project. In addition to the results noted here, the experimental work on this project provided research experience and support for students at Christopher Newport College and provided the basis for one high school science project. Two presentations on the thermodynamics developments have been given: one at the Southeastern Regional Meeting, American Chemical Society, Atlanta, GA, November, 1988; the other at the 198th National Meeting, American Chemical Society, Miami, FL, September, 1989. A discussion session has been planned for the 11th Biennial Conference on Chemical Education, Atlanta, GA, August 5-9, 1990. Copies of publications based on work supported in part or in whole under this grant will be submitted when available.



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